Experimental observation of a torus doubling of a metal/ferroelectric film/semiconductor capacitor

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A metal–ferroelectric–semiconductor (MFS) structure was used as a nonlinear capacitor in a series resonance circuit. The following materials were used as components of the MFS structure: aluminium as the metal electrode, Bi4Ti3O12 film as the ferroelectric, and p-type silicon as the semiconductor. The system was driven by a single frequency at suitably chosen amplitudes. Besides the sequences of period-doubling bifurcations which were already observed in the series resonance circuit with a pure ferroelectric capacitor, we found regions with torus-doubling bifurcations by varying the frequency of the driving voltage at suitably high amplitudes. Comparing the behaviour of the series resonance circuit with a pure ferroelectric capacitor and with the MFS structure, we attribute the reason for the new effect of torus doubling to the properties of the ferroelectric–semiconductor boundary layer.

Keywords: period doubling; torus doubling; metal–ferroelectric–semiconductor structure; nonlinear resonance circuit

1. Introduction

The mechanism of torus doubling has been investigated theoretically and numerically in many papers (e.g. Kaneko 1983, 1984; Venkatesan & Lakshmanan 2001). It was pointed out that this effect may be observed in continuous dynamical systems, but only if they have at least four degrees of freedom. On the other hand, only a few experimental studies on this nonlinear phenomenon can be found in literature. Especially in solid-state physics, ferroelectric materials are good candidates for establishing nonlinear dynamical systems owing to their nonlinear dielectric behaviour (e.g. Lines & Glass 1979). One opportunity to realize a nonlinear dynamical system is a series resonance circuit with a ferroelectric triglycine sulphate (TGS) capacitor (e.g. Diestelhorst & Beige 1988; Beige et al. 1992; Hegger et al. 1998; Kapsch et al. 2001) or a ferroelectric KH₂PO₄ (KDP) capacitor (e.g. Shin 1999; Shin & Kwun 1999). In the case of the TGS capacitor, it

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was shown by Hegger et al. (1998) that the system may be described by a threedimensional flow. Therefore, in such a system, it was possible only to observe period-doubling sequences to chaos. In the KDP-equipped resonance circuit of Shin & Kwun (1999), torus doublings occurred as the KDP introduces additional degrees of freedom. Being specified by a five-dimensional flow, this system yields the possibility for the appearance of a torus doubling.

In our latest experiments, we included a metal–ferroelectric film–semiconductor (MFS) capacitor as a nonlinear element in the series resonance circuit to increase the number of degrees of freedom. Different experiments were performed to characterize the compound material. First, we investigated the dependence of the capacitance on the DC field applied to the material. Then, we investigated the behaviour of the resonance circuit at relatively low driving amplitudes in the vicinity of the resonance frequency. Finally, the behaviour of the system at high amplitudes was observed. In special regions of the parameter space, torus doubling occurred.

2. The MFS structure

The MFS structure used in our experiments is shown in figure 1. It was fabricated by sol-gel deposition of a Bi$_4$Ti$_3$O$_{12}$ film on a p-type silicon wafer with a resistivity of 1–10 $\Omega$ cm. After deposition, the structure was thermally treated in air at 920 K for 30 min. The thickness (286 nm) of the Bi$_4$Ti$_3$O$_{12}$ film has been determined by scanning electron microscopy. X-ray diffraction analysis showed a polycrystalline structure of the ferroelectric layer. Between the ferroelectric film and the Si wafer, there is a SiO$_2$ buffer layer of 5–6 nm thickness. Electrodes were prepared by vacuum evaporation of Al. The lower electrode on the Si wafer was evaporated on the entire surface, whereas the upper one was deposited on the ferroelectric film using a mask. The area of the upper electrodes is approximately 0.25 mm$^2$. Thus, the specimen offers a high number of small capacitors which may be investigated separately or connected to larger capacitors.

3. Experimental results

(a) Capacitance–voltage measurements

Some similarities might be expected between metal oxide semiconductor (MOS) capacitors and the investigated MFS structure, because in principle the dielectric oxide layer of the MOS has been replaced by another special dielectric material—the ferroelectric Bi$_4$Ti$_3$O$_{12}$ film. Therefore, we investigated the dependence of the capacitance of the MFS structure on the applied DC voltage. The measurements were performed using an LCR meter (Agilent 4284A). Figure 2 presents the results of capacitance–voltage (CV) measurements for the following parameters: frequency of the AC voltage $f_{AC} = 35.3$ kHz, r.m.s. value of the AC voltage $U_{AC} = 100$ mV and time rate of change of the DC voltage $\Delta = 3$ mV s$^{-1}$.

It can be clearly seen from figure 2a that, at negative DC voltages, the capacitance increases because the MFS structure reaches the state of accumulation. In this state, the high concentration of very mobile majority carriers in the boundary layer between the ferroelectric film and the p-type Si yields high values of capacitance. At positive DC voltages, i.e. the ferroelectric film is at higher potential...
than the Si, the MFS structure reaches the state of depletion with low capacitance owing to the lack of mobile charge carriers in the boundary layer. This behaviour is well known in terms of MOS capacitors (e.g. Nicollian & Brews 2003). Also the increase of the conductivity (figure 2b) can be explained in this framework. The so-called flatband voltage $U_{\text{FB}}$ marks the threshold between accumulation and depletion. When crossing $U_{\text{FB}}$, accumulated carriers are repelled from or attracted by trap sites near the ferroelectric–silicon surface depending on the direction of crossing. This current leads to a peak in conductivity.

Differing from a typical MOS capacitor, the MFS structure exhibits a hysteresis of the branches during increasing and decreasing of the DC voltage. One possible explanation for this hysteresis could be the ferroelectric switching process. However, experimental evidence might trace it back to be merely originating from an ill-conditioned MOS behaviour. Since trap captures and emissions as well as switching processes were compensated by a current flow, they cannot be distinguished in measurements of conductivity in dependence on DC voltage. As far as CV measurements are concerned, one should keep in mind

Figure 1. The MFS structure.

Figure 2. Experimentally observed dependence of (a) the capacitance and (b) the conductivity on the DC voltage.
that these refer to a differential change of charge $\delta Q$ caused by a small change of the applied voltage $U_{DC} + \delta U$ (i.e. $\delta U = U_{AC}$). Any transients changing the quantity of mobile carriers will appear in a CV measurement as a variation in capacitance, despite being measured at the same bias. Figure 3 shows the influence of the variation rate of the DC voltage on the width of the hysteresis. At low rates, the so-called memory window becomes remarkably narrower, which would argue for a relaxation rather than for the switching of the ferroelectric film. Typical time constants of trap level states can reach up to 1 s (Nicollian & Brews 2003). According to a pulsed CV-measuring procedure at MFS structures (proposed by Yoshimura & Fujimura 2000), avoiding transient effects, there is no ferroelectric contribution at all.

(b) Shift of resonance frequency

As can be concluded from §3a, the MFS structure behaves like a strongly nonlinear capacitor. This fact was used to build a nonlinear series resonance circuit (figure 4). The circuit has been described in more detail in our previous papers (e.g. Diestelhorst & Beige 1988; Diestelhorst et al. 1999; Diestelhorst 2004). Two kinds of investigations were carried out with this nonlinear dynamical system—the investigation of the shift of resonance frequency at relatively low amplitudes of the driving voltage, presented in this subsection, and the investigation of the bifurcation behaviour at higher amplitudes of the driving voltage (see §3c).

Figure 5a presents some resonance curves of the circuit recorded by a spectrum/network analyser (Wandel & Goltermann SNA2). Curve (i) corresponds to the lowest applied driving voltage and curve (ii) corresponds to the highest applied voltage, leading to the occurrence of the jump phenomenon of nonlinear oscillators (e.g. Nayfeh & Mook 1979). The resonance frequency shifts initially to higher values, if the driving voltage is slightly increased at very low amplitudes. A further
increase of the driving voltage amplitude reverses the direction of the resonance frequency shift to lower values. The two differently directed shifts indicate that there must be at least two different mechanisms of nonlinearities in the MFS structure. The reason for that behaviour may be attributed to the properties of the boundary layer between the ferroelectric Bi$_4$Ti$_3$O$_{12}$ film and the p-type silicon. At low amplitudes, the MFS operating point is in the vicinity of $U_{\text{FB}}$. At higher amplitudes, it resides between accumulation and depletion, introducing different mechanisms which cause deviations from the small signal response.

At the same time, there seems to be superimposed a slow relaxation owing to the low mobility of the charge carriers at the transition from deep depletion to accumulation state. This assumption is supported by the observation of a drift of the resonance curves if the amplitude of the driving voltage is kept constant for the time of recording resonance curves several times (see figure 6). The first approach to model an MFS is to simply combine ferroelectric switching (Landau double well potential) and MOS-type behaviour (band-bending model

Figure 4. The series resonance circuit including the connections for recording of the phase portrait.

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according to Nicollian & Brews (2003)):

$$L\ddot{D} + R\dot{D} + \frac{1}{A}\left(U_{FB} + \frac{d_{Ox}D}{\varepsilon_{Ox}} + d_{fe}(\alpha D + \gamma D^3)\right) = \begin{cases} \delta_1 D^2, & \text{if } D \leq 0 \\ \delta_2 \ln D, & \text{if } D > 0 \end{cases} = \frac{U_{ext}}{A}.$$ 

Here, $D$ is the dielectric displacement; $U_{FB}$ is the flat-band voltage; $d_{Ox}$ and $d_{fe}$ are the thicknesses of the buffer layer and the ferroelectric film, respectively; $L$ is the inductance and $R$ is the (linear) losses of the circuit; $A$ is the electrode area and $U_{ext}$ is the driving voltage. The other coefficients represent the linear and nonlinear properties of the ferroelectric film and the boundary layer. Although this model introduces an additional nonlinearity to the pure ferroelectric capacitor setup, preliminary numerical results reveal that it is far from a qualitative description of experimental observations.

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The next experiment was performed at a driving voltage of $U_{\text{AC}} = 7.5 \text{ V}$ at frequencies above the resonance frequency of the circuit. The driving frequency was swept at constant amplitude of the driving voltage from lower to higher values by an HP 3325B generator. Simultaneously, the spectrogram was recorded by an Agilent 89410A vector signal analyser. The result is presented in figure 7a.

The diagram shows the change of driving frequency in time. The blue and green lines indicate the shift of spectral lines if the driving frequency is swept. The height of the peaks is encoded in the colours of the lines. Blue corresponds to high peaks, whereas lower signal intensities and the noise level are coloured yellow and orange, respectively. The numbers at the top of that diagram indicate the driving frequency (1), the peak at the subharmonic frequency (1/2 of the driving frequency) and the peak at 3/2 of the driving frequency at the beginning of the experiment. Starting from the top, the driving frequency is increasing. It should be noted that, at this region, the signal at half the driving frequency is higher than the signal at the driving frequency itself. Then, the system reaches a narrow region of a period-doubling cascade, where signals of 1/4, 1/8 and their higher harmonics may be observed. By further increasing the frequency, a region with a modulation below half the driving frequency arises in the spectrogram. In this region, one can observe a blow up of the phase portrait which was recorded simultaneously by a Nicolet Pro30 digital storage oscilloscope.

Figure 7b presents a two-dimensional projection of the phase portrait recorded from the signals proportional to $D$ and $\dot{D}$ by the oscilloscope in $xy$-mode according to figure 4, when the system was driven with an external frequency of $f_{\text{ext}} = 27.134 \text{ kHz}$. The purple points represent a record sampled with a rate of $f_s = 10 \text{ MHz}$. The green stroboscopic points were recorded at a sampling rate equal to the frequency of the driving voltage $f_{\text{strob}} = f_{\text{ext}}$ resulting in one recorded point per period of driving. The corresponding driving frequency is indicated in the spectrogram. One can see that, in this region, we find the strong signal at half the driving frequency and the modulation at below half the driving frequency. From the two circular regions in the stroboscopic view, one can conclude that the nonlinear system at these parameters is in a state of period-doubled torus. That becomes more obvious if the same data as used in figure 7 are arranged in a three-dimensional projection of the phase space with the period of the external driving as the cyclic coordinate (Guckenheimer & Holmes 1990). Figure 8 presents such a three-dimensional projection constructed from 41 920 data points. As in figure 7b, purple points represent the data recorded at a sampling rate of 10 MHz corresponding to approximately 113 periods of forcing. In figure 8a, the data are presented along the period $T$ of the external voltage. The plane illustrates how the Poincaré map was observed by stroboscopic recording of the signals at the sampling rate equal to the driving frequency of forcing. The green data points at this plane were generated by a separate stroboscopic observation of 41 920 periods of the response of the nonlinear circuit in the torus 2 regime. Obviously, the system needs two periods to return into the region of the starting point. From the Poincaré map, one can see clearly the two circles corresponding to a period-doubled torus. In figure 8b, the same experimental data are used again for constructing another three-dimensional projection of the phase portrait. Now the data are recorded along the doubled period $2T$ of the forcing. One cycle
corresponds to two periods of the external voltage. Hence, the stroboscopic observation of the signals with a sampling rate equal to the driving frequency yields two Poincaré sections, as indicated in that figure.

Each of them represents one of the two regions visible in the Poincaré map shown in figure 8a. From the theory of torus doubling, it is well known that a continuous system that offers torus doubling behaviour must have at least four degrees of freedom. Although there exist theoretical models of flows and maps which show torus doublings in simulation, it has not been possible for us, as mentioned already in §3b, to find a model that could describe the observed effects satisfactorily in the context of our real physical system so far. In our earlier experiments with a series resonance circuit with a nonlinear capacitor containing a pure ferroelectric material as the dielectric, it was shown by Hegger et al. (1998) that three degrees of freedom were sufficient to describe the behaviour of that system correctly. The comparison with these experiments suggests that the additional degree(s) of freedom should be introduced into the resonance circuit by the boundary layer between the ferroelectric material and the semiconductor. They could be a result of relaxational processes of the charge carriers near this surface during the ferroelectric switching and the changing of the MFS structure state between accumulation and depletion.

4. Conclusions

The MFS structure was characterized concerning its nonlinear properties by different methods and at different levels of impact. The CV measurements revealed the influence of the carrier density in the boundary layer. Whereas we could detect the regions of accumulation and depletion of the majority of carriers, we were not able to determine absolutely whether the ferroelectric film was switching or not. The investigation of the shift of resonance frequency revealed the effect of at least two different types of dielectric nonlinearities. The observation of a torus doubling indicates that the behaviour of the resonance

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A circuit with an MFS structure needs a higher dimensional phase space than the circuit with a pure ferroelectric TGS capacitor. Further investigations into the properties of MFS structures, above all the interface trap level distribution, are necessary for a better understanding of the ferroelectric semiconductor interplay and its contribution to the nonlinear phenomena presented here.

References


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Shin, J. C. 1999 Experimental observation of a torus-doubling transition to chaos near the ferroelectric phase transition of a KH2PO4 crystal. *Phys. Rev. E* 60, 5394–5401. (doi:10.1038/311655a0)

